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TECHNICAL MEMORANDUM 1269

ISENTROPIC PHASE CHANGES IN DISSOCIATING GASES AND THE  
METHOD OF SOUND DISPERSION FOR THE INVESTIGATION OF  
HOMOGENEOUS GAS REACTIONS WITH VERY HIGH SPEED

By Gerhard Damköhler

Translation of "Isentropische Zustandsänderungen in Dissoziierenden  
Gasen und die Methode der Schalldispersion zur Untersuchung sehr  
Schneller Homogener Gasreaktionen."  
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ISENTROPIC PHASE CHANGES IN DISSOCIATING GASES AND THE  
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(CONCLUSION)

V. DISPERSION OF SOUND DUE TO SPECIAL PHYSICAL EFFECTS, SUCH AS  
FRICTION, THERMAL CONDUCTIVITY, AND DIFFUSION

## 1. Friction and Heat Conductivity in the Plane, Laterally Unlimited

## Sound Wave According to Kirchhoff (R-W Longitudinal Damping)

Long before the dispersion of sound due to incomplete chemical equilibrium had been discovered, A. R. Kirchhoff<sup>1</sup> had indicated that friction and heat conductivity produced such sound dispersion in any gas at correspondingly high frequencies. His final equation for the quantity  $g$   $[(48)]^2$  in the case of the plane, laterally unlimited sound wave reads:

$$g = \frac{h}{a_0} \sqrt{1 - \frac{h}{a_0^2} \left( \frac{4\nu}{3} + [\kappa - 1] \tau \right)} \quad (146)$$

\*"Isentropische Zustandsänderungen in Dissoziierenden Gasen und die Methode der Schalldispersion zur Untersuchung sehr Schneller Homogener Gasreaktionen. Zeitschrift für Elektrochemie, Bd 48, No. 3, 1942, pp. 116-131. (This paper is a continuation of NACA TM 1268, the equations, tables, and figures being numbered in sequence from that report.)

<sup>1</sup>Kirchhoff, Pogg. Ann. Physik 134, 1868, pp. 177-193.

<sup>2</sup>Numbers in brackets refer to equations in the first part of this paper, TM 1268.

where<sup>3</sup>

$$\left\{ \begin{array}{l} a_0 = \sqrt{\frac{\kappa RT}{M}}, \\ v = \text{kinematic viscosity,} \\ \tau = \text{temperature conductivity} \end{array} \right. \quad (147)$$

Developing the square root of the equation (146) gives in first approximation:

$$g = \frac{2\pi f l}{a} + \gamma \approx \frac{2\pi f l}{a_0} + \frac{(2\pi f)^2}{2a_0^3} \left( \frac{4v}{3} + [\kappa - \frac{1}{2}] \tau \right) \quad (148)$$

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<sup>3</sup>Kirchhoff himself did not use  $\frac{4v}{3}$ , but the sum of the coefficients  $\mu'$  and  $\mu''$  from the friction term  $\mu' \Delta \underline{w} + \mu'' \text{grad div } \underline{w}$  of the flow equation (momentum equation). In the Navier-Stokes equation, it assumes the form  $v \Delta \underline{w} + \frac{v}{3} \text{grad div } \underline{w}$ .

The kinematic viscosity  $v = \frac{\eta}{\rho}$  ( $\eta$  = dynamic viscosity,  $\rho$  = density) is not likely to be taken for the stoichiometric conversion factors, because they invariably carry subscripts. The temperature conductivity  $\tau$  depends upon the thermal conductivity  $\lambda$ , the specific heat  $c_p$ , and the density  $\rho$ , according to the relation  $\tau = \frac{\lambda}{c_p \rho}$ .

When  $z$  denotes the average number of collisions per second which a molecule experiences,  $\frac{h\nu}{a_0^2} \approx \frac{h\nu}{a_0^2} \approx \frac{4\pi f}{z}$ , with it, the order of magnitude of the dimensionless supplementary terms below the square root of equation (146) can be readily estimated from the sound frequency  $f$  and the number of collisions  $z$ .

or in other words, the velocity of sound with respect to the quantity

$a_0 = \sqrt{\frac{kRT}{M}}$  is not changed by the friction and heat conduction. But sound absorption occurs, whereby the damping exponent  $\gamma$  increases proportional to the square of the sound frequency<sup>4</sup>  $f$ , and is also proportional to the quantities  $\nu$  and  $\tau$  describing the exchange of momentum and heat and, lastly, inversely proportional to  $a_0^3$ . The effect of the last two points is that the numerical value of  $\gamma$  varies rather little with the temperature for a given frequency  $f$ , that is, only in the measure of the Sutherland correction and the Prandtl number  $Pr$  because

$$a_0^3 \sim T^{3/2} \quad (149)$$

$$\frac{\nu_T}{273} = \left(\frac{T}{273}\right)^{3/2} \left(\frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}\right); \quad C = \text{Sutherland's constant} \quad (150)$$

$$\tau = \frac{\nu}{Pr} \quad Pr = \text{Prandtl number} \quad (151)$$

The derivation of equation (146), which Kirchhoff gained only by complicated calculations, can be omitted here since it appears in the next section as a special case, wherein the simultaneous concurrence of incomplete chemical equilibrium of friction and heat conduction on the sound wave is treated exact.

However, it is interesting to compute the numerical values resulting from equation (146) for dissociating  $CO_2$  at  $2600^\circ K$  and 1 atmosphere, that is,  $a$ ,  $\gamma$ ,  $\gamma_l$  as well as the ensuing quantities  $e^{-10\gamma}$  and  $e^{-20\gamma}$ .

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<sup>4</sup>Hence there is a difference with respect to the sound absorption caused by kinetic reaction, where  $\gamma$  with rising frequency  $f$  tends toward a constant limiting value (cf. fig. 3c, TM 1268, p. 58).

The kinematic viscosity  $\nu$  of a gas mixture can be approximated by the Mann formula<sup>5</sup> from the kinematic viscosities  $\nu_j$  of the individual gases  $j$  and their molar fractions  $\frac{N_j}{N}$

$$\frac{1}{\nu} = \sum_j \frac{1}{\nu_j} \frac{N_j}{N} \quad (152)$$

For  $T = 273^\circ \text{K}$  we get with  $\nu_{\text{CO}_2} = 0.0692$ ,  $\nu_{\text{CO}} = 0.133$  and  $\nu_{\text{O}_2} = 0.134 \text{ cm}^2/\text{sec}$  with due allowance for the molar fractions according to Table 4,  $\nu_{273^\circ \text{K}} = 0.0783$ . With Sutherland's constant  $C = 235$ , which was calculated additively from the individual values  $C_{\text{CO}_2} = 274$ ,  $C_{\text{CO}} = 101$ , and  $C_{\text{O}_2} = 138$  by the formula  $C = \sum_j C_j \frac{N_j}{N}$ , formula (150) finally gives:

$$\begin{aligned} \nu_{2600^\circ \text{K}} &= 0.0783 \underbrace{\left(\frac{2600}{273}\right)^{3/2}}_{29.4} \underbrace{\left(\frac{1 + \frac{235}{273}}{1 + \frac{235}{2600}}\right)}_{171} \\ &= (3.9 \pm 0.8) \text{ cm}^2/\text{sec} \end{aligned} \quad (153)$$

The limit of error was intentionally put at 20 percent, because the exact validity of Mann's formula (152) and the temperature relationship of  $\nu$  up to  $2600^\circ \text{K}$  according to formula (150) has not been experimentally proved.

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<sup>5</sup>Mann, Gas- u. Wasserfach 73, 570, 1930. See also Rammler, E., and Breitling, K., Bericht E 6, 1937, des Reichskohlenrats: Über die Zähigkeit von Gasen und Gasgemischen sowie ihre Abhängigkeit von der Temperatur.

The temperature relationship  $\tau$  follows then by equation (151) with  $Pr = 0.85 \pm 0.09$  as

$$\tau = \frac{3.9 \pm 0.8}{0.85 \pm 0.09} = (4.6 \pm 1.4) \text{ cm}^2/\text{sec} \quad (154)$$

The insertion of these figures in equation (146) finally gives the data under No. 2 in Table 7, p. 37. They can be compared with those quoted under No. 1 which correspond to the sound dispersion (Table 6, TM 1268, p. 54) caused solely by incomplete chemical equilibrium (Case II:  $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ ). It is seen that, above  $f = 10^5$  cycles per second (cps), Kirchhoff's sound dispersion due to irreversible momentum and heat exchange parallel to the direction of propagation (R-W longitudinal damping) can no longer be neglected.

## 2. Kinetic-Reaction Sound Dispersion and R-W Longitudinal

### Damping in the Plane, Laterally Unlimited Sound Wave

What values are to be expected for the velocity and the absorption of sound, when kinetic reaction and Kirchhoff sound dispersion are superposed by R-W longitudinal damping? For the  $\gamma$  values, simple additivity might be assumed in first approximation, which would then afford the data shown under No. 3 of Table 7. For the sonic velocity  $a$ , the numerical value due to kinetic reaction alone might be suspected, although this is much more uncertain, since the concurrence of the two causes of dispersion might be accompanied by special effects. However, this is to be checked on the basis of a relation derived from equation (146), with due regard to the incomplete chemical equilibrium, friction, and heat conduction.

Proceeding from the laws of the conservation of mass, energy, and momentum, that is, from the equations [(41)] to [(46)], the energy and momentum equation are extended to include the heat-conduction and the friction term, thus replacing equations [(44)] and [(45)] by the new energy equation

$$\frac{dE}{dt} = -p \frac{dV}{dt} + v\lambda \frac{\partial^2 \tau}{\partial x^2} \quad (155)$$

and

$$c_p \frac{dT}{dt} - v \frac{dp}{dt} - \sum_m w_m \frac{dz_m}{dt} - v\lambda \frac{\partial^2 T}{\partial x^2} = 0 \quad (156)$$

and the previous Euler equation [(46)] is replaced by the new momentum equation of Navier-Stokes:

$$\rho \frac{dw}{dt} = -\frac{\partial p}{\partial x} + \rho \frac{4\nu}{3} \frac{\partial^2 w}{\partial x^2} \quad (157)$$

The expressions on the left-hand side of [(47)] are entered in equation (156); the entire equation is divided by the constant quantity  $p_0 V_0 = N_0 R T_0$ ; the relative temperature variation  $\frac{\delta T}{T_0} \approx \frac{\delta T}{T}$  is expressed by equation (16) again; the separate differentiations are affected by utilizing the right-hand expressions [(47)]; and, lastly, the temperature conductivity

$$\tau = \frac{\lambda}{c_p \rho} = \frac{V_0 \lambda}{C_p} = \frac{V_0 \lambda (\kappa - 1)}{N_0 R \kappa} \quad (158)$$

is introduced in place of the heat conductivity  $\lambda$ .

The calculation (all small terms of second or higher order being disregarded) gives then the energy equation

$$\begin{aligned} \kappa \left( 1 - \frac{g^2}{h} \tau \right) \frac{v}{V_0} + \left( 1 - \frac{g^2}{h} \kappa \tau \right) \frac{p}{p_0} \\ + \sum_m \left( A_m - \frac{g^2}{h} \kappa \tau v_m \right) \frac{z_m}{N_0} = 0 \end{aligned} \quad (159)$$

which, together with the unaltered lower  $n$  gross reaction equations of the system [(69)]

$$(A_l + \kappa C_l) \frac{v}{V_0} + C_l \frac{p}{p_0} + \sum_m B'_{lm} \frac{z_m}{N_0} = 0 \quad (160)$$

with  $B'_{lm}$  defined by equations [(71)], [(72)], and [(23)] again forms an equation system from which the ratio  $\frac{p}{p_0} \frac{V_0}{v}$  can be immediately computed.

Hence,

$$\frac{-p}{p_0} \frac{V_0}{Y} = \frac{\begin{vmatrix} \kappa \left(1 - \frac{g^2}{h}\right) \left(A_1 - v_1 \frac{g^2}{h} \kappa \tau\right) \left(A_2 - v_2 \frac{g^2}{h} \kappa \tau\right) \dots \left(A_n - v_n \frac{g^2}{h} \kappa \tau\right) \\ (A_1 + \kappa C_1) & B'_{11} & B'_{12} & \dots & B'_{1n} \\ (A_2 + \kappa C_2) & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (A_n + \kappa C_n) & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix}}{\begin{vmatrix} \left(1 - \frac{g^2}{h} \kappa \tau\right) \left(A_1 - v_1 \frac{g^2}{h} \kappa \tau\right) \left(A_2 - v_2 \frac{g^2}{h} \kappa \tau\right) \dots \left(A_n - v_n \frac{g^2}{h} \kappa \tau\right) \\ C_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ C_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ C_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix}} \quad (161)$$

The first term at the left above in the numerator determinant can be decomposed in two summands

$$\kappa \left(1 - \frac{g^2}{h} \tau\right) = \kappa \left(1 - \frac{g^2}{h} \kappa \tau\right) + (\kappa - 1) \frac{g^2}{h} \kappa \tau \quad (162)$$



But with it the numerator determinant can be represented as sum of two determinants of which one is the determinant of the denominator multiplied by  $\kappa$ . Hence, after division:

$$\frac{-p}{p_0} \frac{V_0}{Y} = \kappa + \frac{\begin{vmatrix} (\kappa - 1) \frac{g^2}{h} \kappa \tau & (A_1 - v_1 \frac{g^2}{h} \kappa \tau) & (A_2 - v_2 \frac{g^2}{h} \kappa \tau) & \dots & (A_n - v_n \frac{g^2}{h} \kappa \tau) \\ A_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ A_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ A_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix}}{\begin{vmatrix} (1 - \frac{g^2}{h} \kappa \tau) & (A_1 - v_1 \frac{g^2}{h} \kappa \tau) & (A_2 - v_2 \frac{g^2}{h} \kappa \tau) & \dots & (A_n - v_n \frac{g^2}{h} \kappa \tau) \\ C_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ C_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ C_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix}} \quad (163)$$

The determinants are introduced

$$\Delta'_1 = \begin{vmatrix} 0 & A_1 & A_2 & \dots & A_n \\ A_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ A_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ A_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix} \quad (164)$$

$$\Delta'_2 = \begin{vmatrix} 1 & A_1 & A_2 & \dots & A_n \\ C_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ C_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix} \quad (165)$$

$$\Delta'_3 = \begin{vmatrix} (\kappa - 1)(-v_1)(-v_2) \dots (-v_n) \\ A_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ A_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \vdots & \vdots & \vdots & & \vdots \\ A_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix} \quad (166)$$

$$\Delta'_4 = \begin{vmatrix} 1 & v_1 & v_2 & \dots & v_n \\ C_1 & B'_{11} & B'_{12} & \dots & B'_{1n} \\ C_2 & B'_{21} & B'_{22} & \dots & B'_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B'_{n1} & B'_{n2} & \dots & B'_{nn} \end{vmatrix} \quad (167)$$

The first two (164) and (165) are those already met in [(70)]. If no shifting chemical equilibria are present in the gas:

$$\Delta'_1 \rightarrow 0 \quad \Delta'_2 \rightarrow 1 \quad \Delta'_3 \rightarrow (\kappa - 1) \quad \Delta'_4 \rightarrow 1 \quad (168)$$

For (163)

$$\frac{-p}{p_0} \frac{v}{v_0} = \kappa + \frac{\Delta'_1 + \frac{g^2}{h} \kappa \Delta'_3}{\Delta'_2 - \frac{g^2}{h} \kappa \Delta'_4} \quad (169)$$

When the quantity  $\frac{g^2}{h} \kappa$  is sufficiently small, the equation [(70)] results, as is to be expected.

However, the ratio  $\frac{-p}{p_0} \frac{v}{v_0}$  can then also be computed from the hydrodynamic continuity and momentum equations, that is, from equations [(43)] and (157)

$$h \frac{v}{v_0} = g w \quad (170)$$

$$\rho_0 \left( h - \frac{4v}{3} g^2 \right) w = -g p \quad (171)$$

or, after removal of  $w$ ,

$$\frac{-p}{p_0} \frac{v}{v_0} = \frac{1 - \frac{4v}{3} \frac{g^2}{h}}{\frac{p_0}{\rho_0} \frac{g^2}{h^2}} \quad (172)$$

Equating (169) to (172) gives

$$\left( 1 - \frac{4v}{3} \frac{g^2}{h} \right) \left( \Delta'_2 - \frac{g^2}{h} \kappa \Delta'_4 \right) = \frac{p_0 g^2}{\rho_0 h^2} \left( \Delta'_1 + \kappa \Delta'_2 + \frac{g^2}{h} \kappa [\Delta'_3 - \kappa \Delta'_4] \right) \quad (173)$$

that is, an equation with which  $g$  can be determined as function of  $h$ .

Equation (173) is solved again, while small terms of the second or higher order are disregarded, by putting

$$g = g_o(1 + y) \quad (174)$$

quantity  $g_o$  is assumed to be the numerical value resulting from equation (173) for vanishing kinetic reaction and vanishing Kirchhoff sound dispersion, that is, when in equation (173),

$$\nu \rightarrow 0 \quad \tau \rightarrow 0 \quad \Delta'_1 \rightarrow 0 \quad \Delta'_2 \rightarrow 1 \quad \Delta'_3 \rightarrow (\kappa - 1) \quad \Delta'_4 \rightarrow 1 \quad (175)$$

But in that case

$$1 = \frac{p_o g_o^2 \kappa}{\rho_o h^2} \quad (176)$$

or, after introduction of

$$a_o = \sqrt{\frac{\kappa p_o}{\rho_o}} = \sqrt{\frac{\kappa R T_o}{M}} \quad (177)$$

$$g_o = \frac{h}{a_o} \quad (178)$$

and

$$\frac{g^2}{h} = \frac{h}{a_o^2} (1 + y)^2 \quad (179)$$

With it (173) becomes

$$\begin{aligned} \Delta'_2 - \left( \frac{4\nu}{3} \Delta'_2 + \tau \kappa \Delta'_4 \right) \frac{h}{a_o^2} (1 + y)^2 \\ = \underbrace{\frac{p_o}{\rho_o a_o}}_{\frac{1}{\kappa}} (1 + y)^2 \left( \Delta'_1 + \kappa \Delta'_2 + \frac{h}{a_o^2} (1 + y)^2 \kappa \tau [\Delta'_3 - \kappa \Delta'_4] \right) \end{aligned} \quad (180)$$

or

$$\begin{aligned} \kappa \Delta'_2 - \frac{\kappa h}{a_0^2} \left( \frac{4v}{3} \Delta'_2 + \tau \kappa \Delta'_4 \right) \\ = (1+y)^2 (\Delta'_1 + \kappa \Delta'_2) + \frac{\kappa h}{a_0^2} \tau (\Delta'_3 - \kappa \Delta'_4) \end{aligned} \quad (181)$$

or

$$(1+y) = \sqrt{\frac{\kappa \Delta'_2}{\Delta'_1 + \kappa \Delta'_2} - \frac{\kappa h}{a_0^2} \frac{\left( \frac{4v}{3} \Delta'_2 + \tau \Delta'_3 \right)}{(\Delta'_1 + \kappa \Delta'_2)}} \quad (182)$$

For  $g = \frac{\bar{h}}{a_0} (1+y)$ , it finally gives

$$\left\| g = \frac{\bar{h}}{a_0} \sqrt{\frac{\kappa}{\left( \kappa + \frac{\Delta'_1}{\Delta'_2} \right)} \left[ 1 - \frac{h}{a_0^2} \left( \frac{4v}{3} + \tau \frac{\Delta'_3}{\Delta'_2} \right) \right]} \right\| \quad (183)$$

which is the final formula for the case when the Kirchhoff sound dispersion and that due to kinetic reaction are superposed in the plane, laterally unlimited sound wave (RW - longitudinal damping). For vanishing Kirchhoff dispersion, that is, for  $v \rightarrow 0$  and  $\tau \rightarrow 0$ ,

$$g = \frac{\bar{h}}{a_0} \sqrt{\frac{\kappa}{\kappa + \frac{\Delta'_1}{\Delta'_2}}} \quad (184)$$

which is identical with equation [(77)]. For vanishing dispersion due to kinetic reaction,  $\frac{\Delta'_1}{\Delta'_2} = 0$  and  $\frac{\Delta'_3}{\Delta'_2} = \kappa - 1$ , which is identical with equation (146).

The sound dispersion values computed for dissociating  $\text{CO}_2$  at  $2600^\circ \text{K}$  and 1 atmosphere by equation (183) are reproduced under No. 4 in Table 7. They do not differ as regards sound absorption within the calculating accuracy from the data under No. 3; that is, the damping constant  $\gamma$  can be tolerably well approximated from the pure kinetic reaction damping constant and the damping constant of pure Kirchhoff sound dispersion. Within mathematical accuracy, the sonic velocity  $a$  of No. 4 is identical with the sonic velocity for pure kinetic reaction dispersion, and so confirms the previously expressed suspicions concerning the sound absorption and the sonic velocity at superposition of kinetic reaction - and Kirchhoff sound dispersion.

### 3. Kinetic-Reaction Sound Dispersion and R-W Longitudinal

#### Damping in the Plane, Laterally Unlimited Sound Wave

##### with Simultaneous Allowance for Diffusion

The foregoing examples have shown that above  $10^5$  cps, both the Kirchhoff and the kinetic reaction dispersion must be taken into consideration. The former consists in the fact that, at these high sound frequencies and hence correspondingly short wave lengths, the momentum and temperature differences between adjacent wave crest and trough during one cycle already start perceptibly to balance. If the chemical composition of the gas is the same at every instant (constant molar fractions in time) as is invariably the case in the absence of chemical reactions, the exchange of momentum by friction and the exchange of heat by conduction are actually the only irreversible transport processes of this kind that can produce the sound dispersion. But the conditions are different in the presence of chemical reactions. Concentration differences occur between wave crest and wave trough, especially when the chemical reactions are still able to follow the sound frequency, so that an irreversible particle exchange by diffusion must also be taken into account. Whether its effect on sound dispersion is greater or smaller than friction and thermal conduction is impossible to predict beforehand. In consequence, an exact formula must be derived in which, aside from the factors causing the dispersion, the diffusion is also considered.

Of the initial equations [(41)] to [(46)], the equations of continuity remained unaltered. They are now supplemented by diffusion terms. Thus equation [(41)] becomes

$$\frac{dN_j}{dt} = - \sum_m v_{jm} \frac{dz_m}{dt} + v \frac{\partial}{\partial x} \left[ D \frac{N}{V} \frac{\partial}{\partial x} \left( \frac{N_j}{N} \right) \right] \quad (185)$$

It is to be noted that the number of moles  $\vec{N}_j$  diffused through 1 cm<sup>2</sup> per second in x direction in the nonisothermal field is not given by

$$\vec{N}_j = -D \frac{\partial c_j}{\partial x} \quad (186)$$

$$\left( [D] = \frac{\text{cm}^2}{\text{sec.}} \quad [c_j] = \frac{\text{mole } j}{\text{cm}^3} \right)$$

but by the expression

$$\vec{N}_j = -cD \frac{\partial}{\partial x} \left( \frac{N_j}{N} \right) \quad (187)$$

with

$$c = \sum_j c_j = \frac{\text{total number of moles}}{\text{cm}^3}$$

For, at validity of equation (186), a change in the composition of the gas due to diffusion could occur in the nonisothermal field, even if originally the molar fractions are everywhere the same; however, such changes in gas composition certainly do not occur in first approximation on the basis of the pure diffusion coefficient  $D$ , but at the most in second approximation, because of thermodiffusion, which is, however, disregarded here.

Equation (187) can also be derived by the kinetic gas theory. Bearing in mind in (185) that

$$\frac{N_j}{N} = \frac{N_{j0} \left( 1 + \frac{\delta N_j}{N_{j0}} \right)}{N_0 \left( 1 + \frac{\delta N}{N_0} \right)} \approx \frac{N_{j0}}{N_0} \left( 1 + \frac{\delta N_j}{N_{j0}} - \frac{\delta N}{N_0} \right) \quad (188)$$

we get

$$\frac{dN_j}{dt} = - \sum_m v_{jm} \frac{dz_m}{dt} + D \frac{\partial^2}{\partial x^2} \left( \delta N_j - \frac{N_{j0}}{N_0} \delta N \right) \quad (189)$$

for identical diffusion coefficient  $D$  and omission of the small terms of higher order, and by summation over all types of particles  $j$

$$\frac{dN}{dt} = - \sum_m v_m \frac{dz_m}{dt} \quad (190)$$

In the last equation, the diffusion term has disappeared because the diffusion did not alter the total number of particles in a volume element, but merely the composition.

Reinsertion of the expressions  $[(47)]$ , followed by differentiation, gives

$$\underline{R} = - \sum_m v_m \underline{z}_m \quad (191)$$

$$\underline{R}_j \left( 1 - \frac{g^2}{h} D \right) = - \sum_m \left( v_{jm} - v_m \frac{N_{j0}}{N_0} \frac{g^2}{h} D \right) \underline{z}_m \quad (192)$$

The third continuity equation  $[(43)]$  (hydrodynamical) remains the same, if by  $V$  is meant, as before, a volume in which the diffusion according to equation (190) is not accompanied by a change in the total number of particles.<sup>6</sup>

The energy equation (155) and the subsequent equations of section V, article 2 are not affected by the inclusion of the diffusion, since the heat conductivity itself, viewed from the gas kinetics standpoint, is nothing but a diffusion of dissimilarly "hot" molecules.

<sup>6</sup>Now it should be readily apparent why  $\frac{1}{V} \frac{dV}{dt} = \frac{\partial w}{\partial x}$  rather than  $\frac{dp}{dt} = -\rho \frac{\partial w}{\partial x}$  was chosen as hydrodynamic continuity equation; because the density (as well as the momentum) in a volume element can well vary by diffusion of heavier or lighter molecules (cf. equation 193).



The inclusion of the diffusion in the momentum equation (157) would theoretically introduce additional terms, as already indicated by Ackermann<sup>7</sup> on the example of the carburization boundary layer. The diffusion in unit time through the unit of surface perpendicular to the X-direction produces the following momentum transport:

$$\vec{J} = \sum_j (M_j w) \underset{\uparrow}{D} \underset{\uparrow}{\frac{N}{V} \frac{\partial}{\partial x} \left( \frac{N_j}{N} \right)} \quad (193)$$

But in view of its dependence as the square of the sound amplitude, as indicated by the arrows, it may be discounted in the first approximation, and the unaltered Navier-Stokes momentum equation (157) retained.

Since the continuity equations for the individual particle types  $j$  have changed with the inclusion of the diffusion, the  $n$  equations [(60)] will no longer result in the equations [(66)] or the lower  $n$  equations of the system [(69)] (identical with equations (160)), but present additional terms in the dimensionless constants, such as  $B'_{lm}$ , for instance, which must be proportional to  $\frac{g^2}{h} D$ .

By [(60)]

$$\begin{aligned} \frac{\vec{U}_l - \bar{U}_l}{U_l} &= \frac{N}{U_l V} \frac{1}{N} \frac{dz_l}{dt} \\ &= - \left( \frac{W_l}{RT} - v_l \right) \left( \frac{\delta p}{p} + \frac{\delta V}{V} + \sum_m v_m \frac{\delta z_m}{N} \right) + \sum_j v_{jl} \left( \frac{\delta N_j}{N_j} - \frac{\delta V}{V} \right) \quad (194) \end{aligned}$$

or after introduction of [(47)] and allowance for (192)

$$\begin{aligned} \frac{2\pi f l N}{U_l V} \left( \frac{z_l}{N} \right) &= - \left( \frac{W_l}{RT} \right) \frac{V}{V} - \left( \frac{W_l}{RT} - v_l \right) \frac{p}{p} - \\ &\quad \sum_m \left( \frac{W_l}{RT} v_m - v_l v_m \right) \frac{z_m}{N} - \sum_j \frac{v_{jl} N}{N_j} \sum_m \frac{\left( v_{jm} - v_m \frac{N_j}{N} \frac{g^2}{h} D \right)}{\left( 1 - \frac{g^2}{h} D \right)} \frac{z_m}{N} \quad (195) \end{aligned}$$

<sup>7</sup>Ackerman, G., VDI-Forschungsheft 382 (1937).

or by disregarding higher powers of  $\frac{g^2}{h}$  D:

$$0 = (A_l + \kappa C_l) \frac{v}{V} + C_l \frac{p}{p} +$$

$$\sum_m \left( i\phi_{lm} + \frac{W_l}{RT} v_m - v_l v_m + \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} + \right.$$

$$\left. \frac{g^2}{h} D \left[ -v_l v_m + \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} \right] \right) \frac{zm}{N} \quad (196)$$

After introducing the new dimensionless abbreviation

$$\left. \begin{aligned} B''_{lm} &= \left( \frac{W_l}{RT} v_m + \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} - v_l v_m \right) + \\ &\quad i\phi_{lm} + \frac{g^2}{h} D \left( \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} - v_l v_m \right), \\ B''_{lm} &= B_{lm} + i\phi_{lm} + \\ &\quad \frac{g^2}{h} D \left( \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} - v_l v_m \right) \\ B''_{lm} &= B'_{lm} + \frac{g^2}{h} D \left( \sum_j^j v_{jl} v_{jm} \frac{N}{N_j} - v_l v_m \right) \end{aligned} \right\} \quad (197)$$

the n relations follow as

$$[A_l + \kappa C_l] \frac{v}{V} + C_l \frac{p}{p} + \sum_m B''_{lm} \frac{zm}{N} = 0 \quad (198)$$

They form, together with the equation (159) unchanged by diffusion, a system of equations which is to be solved with respect to  $\frac{-pV}{pV}$ .

Similarly to (169) follows

$$\frac{-pV}{pV} = \kappa + \frac{\Delta''_1 + \frac{g^2}{h} \kappa \tau \Delta''_3}{\Delta''_2 - \frac{g^2}{h} \kappa \tau \Delta''_4} \quad (199)$$

where the determinants  $\Delta''$  are formed exactly as the determinants  $\Delta'$ , that is, corresponding to equations (164) to (167), except that  $B_{lm}''$  replaces  $B_{lm}'$ .

Since the hydrodynamic equations (170) and (171) can be taken over unchanged, the elimination of  $\frac{-pV}{pV}$  from (172) and (199) leaves, analogous to (183), the final formula

$$\left\| g = \frac{\bar{h}}{a_0} \sqrt{\left( \frac{\kappa}{\kappa + \frac{\Delta''_1}{\Delta''_2}} \right) \left[ 1 - \frac{h}{a_0^2} \left( \frac{4}{3} + \tau \frac{\Delta''_3}{\Delta''_2} \right) \right]} \right. \quad (200)$$

This equation (200) must be solved by successive approximation, since for a given  $h$ , the  $g$  to be found from (200) is also contained in the terms  $B_{lm}''$  of the determinant  $\Delta''$ . However, this approximation

should be easy to do in many cases; for, in the example of the assumed  $\text{CO}_2$  dissociation in Table 7, no difference between the dispersion data under Nos. 5 and 4 computed with and without diffusion can be observed.<sup>8</sup> In other cases the conditions may be similar, so that the use of the  $g$  and  $\frac{g^2}{h}$  values temporarily taken from (183)

frequently represents a very good approximation. Admittedly, the complete agreement of Nos. 4 and 5 in Table 7 seems rather strange; for the friction and heat conductivity are quite considerable in the frequency range of  $10^5$  to  $10^7$  cps, and the diffusion is, gas-kinetically, an irreversible transport process of entirely equal type. The reason is to be found in the fact that at these frequencies either the average diffusion period  $t_D$  for the passage of the particles through a half wave length is substantially greater than their life period, which here is characterized by the half vibration period  $t_s$ , or else that for the

case  $\frac{t_D}{t_s} \leq 1$  the chemical reactions can already no longer follow the sound frequency and thus along the sound wave the molar fractions  $\frac{N_1}{N}$  remain constant in time and space. We obtain

$$\left\| \frac{t_D}{t_s} \approx \left(\frac{l}{2}\right)^2 \frac{1}{2D} \left(\frac{2a}{l}\right) = \frac{la}{4D} = \frac{a^2}{4Df} \right. \quad (201)$$

The thus computed  $\frac{t_D}{t_s}$  values are given at the bottom of Table 7.

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<sup>8</sup>The calculation was made with the diffusion coefficient  $D_{2600} = (7.0 \pm 2.0) \text{ cm}^2/\text{sec.}$ , which had been obtained with Sutherland's formula for the free path length from the value  $D_{273} = 0.14 \text{ cm}^2/\text{sec.}$

applicable at  $273^\circ \text{ K}$  and 1 atmosphere. Thus the ratio is  $\frac{\text{kinematic viscosity}}{\text{diffusion coefficient}} = \frac{\nu}{D} = \frac{3.9}{7.0} \approx 0.56$ , while the Prandtl number

is  $\text{Pr} = \frac{\text{kinematic viscosity}}{\text{temperature conductivity}} = \frac{\nu}{\tau} = 0.85$ . No exact equality exists

between the quantities  $D$ ,  $\nu$ ,  $\tau$ , even for gases, presumably because of the different effect of the persistence of the molecular speeds. See also J. H. Jeans, *Dynamische Theorie der Gase*, Braunschweig 1926, pp. 331 ff, 349f, 380, and 397f.

#### 4. Friction and Heat Conductivity at Sound Propagation in a

##### Smooth-Walled Pipe (G. Kirchhoff)

According to equation (148), the sonic velocity in a plane, laterally unlimited sound wave is not affected at all by friction and heat conductivity, and the damping constant itself is affected very little, when no rather high frequencies ( $f > 10^5$  cps) are utilized. Consequently friction and heat conductivity introduce only small correction terms of the second order. But in a pipe of finite transverse dimensions, the conditions are entirely different. In this case, not only a transport of momentum and heat, largely parallel to the direction of propagation of sound (R-W longitudinal damping), but also a transport cross-wise to it, is involved, because the tangential as well as the normal component of the velocity vector must disappear at the pipe wall and the gas itself must absorb the constant temperature impressed on the wall; in other words, all periodic phase changes in the gas elements directly adjacent to the pipe wall are infinitely small and as a result these elements will experience an irreversible momentum and heat exchange with those located more toward the axis of the pipe. The sound wave receives an additional damping, termed R-W lateral damping.

The problem of the sound wave in a smooth pipe with allowance for friction and heat conductivity (but with kinetic-reaction damping due to incomplete equilibrium disregarded) was treated exact by G. Kirchhoff,<sup>9</sup> after Helmholtz's<sup>10</sup> earlier discussion of the effect of friction. Kirchhoff's calculation is also reproduced in Lord Rayleigh's "Theory of Sound."<sup>11</sup>

The boundary conditions of the sonic field at the pipe wall (speed = 0, temperature = const.) can be defined exact only on the very wide or very narrow pipe, where the concepts wide and narrow are expressed by the numerical values of the dimensionless quantities

$$r \sqrt{\frac{2\pi f}{v}} \approx r \sqrt{\frac{2\pi f}{\tau}} \approx \begin{cases} > 10 & \text{wide pipe} \\ < 1 & \text{narrow pipe} \end{cases} \quad (202)$$

<sup>9</sup>Pogg. Ann. Physik 134, 1868, pp. 177-193.

<sup>10</sup>Helmholtz, H., Verhandlg. des naturhistorisch-medizinischen Vereins zu Heidelberg, Bd. III, pp. 16 to 20. Conference on Feb. 27, 1863.

<sup>11</sup>Strutt, John William, and Rayleigh, Baron, The Theory of Sound, p. 319 ff. 2 Aufl. London 1929.

( $r$  = pipe radius,  $f$  = sound frequency,  $\nu$  = kinematic viscosity,  $\tau$  = temperature conductivity.) If one of these cases prevails and the effect of the R-W longitudinal damping (which resulted precisely in formulas (146) and (148)) is purposely disregarded, the sonic velocity  $a$  and the damping constant  $\gamma$  of the sound amplitude due to the R-W lateral damping, follows as

$$\text{for } r \sqrt{\frac{2\pi f}{\nu}} > 10 \quad \left\{ \begin{array}{l} a = a_0 \left[ 1 - \frac{\sqrt{\nu} + (\kappa - 1)\sqrt{\tau}}{2r\sqrt{\pi f}} \right] \\ \gamma = \frac{\sqrt{\pi f} [\sqrt{\nu} + (\kappa - 1)\sqrt{\tau}]}{ra_0} \end{array} \right. \quad (203)$$

$$\text{for } r \sqrt{\frac{2\pi f}{\nu}} < 1 \quad \left\{ \begin{array}{l} a = a_0 r \sqrt{\frac{\pi f}{2\kappa\nu}} \\ \gamma = \frac{\sqrt{8\pi f \kappa \nu}}{ra_0} \end{array} \right. \quad (204)$$

where, as before,  $a_0 = \sqrt{\frac{\kappa RT}{M}}$  is the sonic velocity in the laterally unlimited medium, if no kinetic reaction sound dispersion prevails. The equations (205) and (206) of the second case are of no interest within the framework of the present report, since they describe the propagation of sound in capillary tubes of  $10^{-3}$  cm or less inside width; merely the quantity  $r \sqrt{\frac{2\pi f}{\nu}}$  with rationally assumed numerical values of  $\nu$  and  $f$  needs to be computed.<sup>12</sup>

The equations (203) and (204) were evaluated for the case of high-temperature dissociation and the data compiled in Table 8.

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<sup>12</sup>The equations (205) and (206) are used in the calculation of the sound-absorption capacity of porous walls, when the pores have the cited dimensions; (see footnote 11, page 328 ff.)

The sonic velocity  $a$  in the pipe is lower than in the laterally unlimited plane sound wave. The corresponding difference  $\frac{a_0 - a}{a_0}$  is so much greater as the pipe is narrower, as the frequency  $f$  is lower, and  $\nu$  and  $\tau$  are higher, that is, as the pressure is lower and the temperature higher. This should be borne in mind when making sound dispersion measurements in the audible frequency range at high temperatures, hence, under conditions likely to be of particular promise for the kinetic investigation of dissociation reactions.<sup>13</sup> Consider a pipe 2 cm in width in contrast with past sound dispersion measurements

$$f \approx 10^5 \text{ sec.}^{-1}$$

$$\nu \approx \tau \approx 0.09 \text{ cm}^2/\text{sec.} \quad \frac{a_0 - a}{a_0} \approx 3.5 \times 10^{-4} \quad (207)$$

and audible range in the high-temperature zone

$$f \approx 10^3 \text{ sec.}^{-1}$$

$$\nu \approx \tau \approx 4 \text{ cm}^2/\text{sec} \quad \frac{a_0 - a}{a_0} \approx 2 \times 10^{-2} \quad (208)$$

Thus, in the past ultrasonic dispersion measurements in gases, a pipe correction could be, in general, omitted. But at audible sound frequencies in the high-temperature range, it must be taken into consideration.

According to equation (204) the portion of the damping constant  $\gamma$  due to the finite width of the pipe (R-W lateral damping) is so much greater as the pipe is narrower, the frequency higher, and the temperature higher. The frequency effect for the damping constant  $\gamma$  is therefore inversely proportional to that of the sonic velocity correction  $\frac{a_0 - a}{a_0}$ .

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<sup>13</sup>And principally for two reasons: on the one hand, little sound absorption, on the other, less interference by oscillation dispersion, (section VI).

The  $\gamma$  value following from equation (204) varies a little with the temperature for one and the same gas; because the quantities  $\sqrt{v}$  and  $\sqrt{\tau}$  in the numerator are proportional to  $T^{3/4}$  up to  $T$ , while the sonic velocity in the denominator is  $a_0 \sim T^{1/2}$ ; therefore the  $\gamma$  value applicable to the R-W lateral damping exhibits a slightly greater temperature effect than that in equation (148) applicable to the R-W longitudinal damping, which was practically independent of the temperature.

#### 5. Comparison of the Damping Constants $\gamma$ For Pure Kinetic

##### Reaction Sound Dispersion, for Pure T-W Longitudinal

##### Damping and Pure R-W Lateral Damping

In connection with figure 3d (TM 1268) it already had been pointed out that, for sound dispersion measurements in the high-temperature range, the sound absorption due to kinetic reaction can impose an upper limit on the frequency range accessible to the measurement. The next problem is to ascertain whether and to what extent the purely physical effects of the R-W longitudinal and lateral damping are involved. In figure 4 the damping constants  $\gamma$  are represented as function of the frequency  $f$  for the following individual cases:

Curves I and II are plotted on the basis of the data in Table 6 (TM 1268) and correspond to the estimated cases I and II of pure kinetic reaction sound dispersion of the dissociating  $\text{CO}_2$  at 2600° K and 1 atmosphere. Curve III is computed on the basis of equation (146) (cf. Table 7) and describes the effect of pure R-W longitudinal damping in the plane, laterally unlimited sound wave.

Curves IV are computed by equation (204) (cf. Table 8) and present the pure R-W lateral damping in the smooth-walled pipe.

Disregarding for a moment the curves I and II, that is, on considering a gas without any dispersion due to kinetic reaction, the entire sound absorption at low frequencies is defined solely by the curves IV, that is, by the R-W lateral damping. But with increasing frequencies, the curve III assumes values no longer negligible and ultimately the  $\gamma$  values of the curve III become even substantially greater than those of curve IV. Thus the R-W longitudinal damping regarded at first as correction term of the second order in the Kirchhoff calculation for the pipe and therefore ignored actually exceeds the R-W lateral damping at certain frequencies. In this range, the total R-W damping in the pipe can then, however, no longer be described by equation (204). The corresponding branches of the curves are therefore indicated by dashes in figure 4. Even so, a not altogether wrong estimate of the R-W



damping can most likely be obtained by following the curves IV at low frequencies, and then changing, at higher frequencies, to the curves III as indicated in figure 4. On the transitional branches,  $\gamma = \gamma_{III} + \gamma_{IV}$  was assumed additionally.

Where is the upper limit of the experimentally accessible frequency range if it were defined by the R-W damping of a smooth-walled pipe alone? Conducting the sound over a path length of only 10 cm into the actual test chamber, while the sound intensity is not to drop more than 0.13 times its original value, should give

$$e^{-2\gamma \times 10} \geq 0.13 \quad \text{and hence} \quad \gamma \leq 0.1 \quad (209)$$

So, if the sound-inlet pipe had an inside width of 6 mm, for reasons of minimum thermal reflection of the hot test chamber, the upper limit of the experimentally still accessible frequency range would lie at around  $2 \times 10^5$  cps, according to figure 4. Such a case would still be compatible with an additive kinetic reaction dispersion, as represented by curve I, but no longer with one such as case II, where the kinetic reaction damping alone would already contribute a greater proportion to the total  $\gamma$  than the R-W damping.

In the evaluation of the total damping constant, it was assumed to be built up additively from the values for pure kinetic reaction damping, for pure R-W longitudinal damping, and pure R-W lateral damping. This actually holds largely for the plane, laterally unlimited sound wave, where the last type of damping cancels out, as indicated by the numerical values of Table 7. But no exact statement regarding the conditions in a pipe of finite inside width is as yet possible. Still, there is no physical basis for any marked departures from the additivity, hence the following conclusion:

Sound-dispersion measurements in the high-temperature range above  $10^5$  cps are scarcely feasible, unless they succeed in producing sound of definite frequencies in the hot test chamber itself, where the sound would not have to travel the minimum distance of 10 cm, but perhaps only a few wave lengths. Ten wave lengths cover about 0.8 cm at  $10^6$  cps according to Table 6, TM 1268.

In point of fact, Sherratt and Griffiths<sup>14</sup> were unable to effect sound measurements in CO<sub>2</sub> of 1000° C even at 27 kcps, on account of excessive absorption. They applied the acoustic interferometer method to a pipe of 1.5-cm inside width and 130-cm length. The oscillating

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<sup>14</sup>Sherratt, G. G. and Griffiths, E., Proc. Roy. Soc., London (A) 156, pp. 504 to 517, 1936.

quartz producing the sound was, of course, located outside of the high-temperature zone, since it would be subjected to transformation to  $\alpha$  quartz at a mere 575° C. The findings by Sherratt and Griffiths are readily intelligible on the basis of figure 4. But the knowledge of the diversified damping effects also refers to another point, heretofore perhaps not always observed in suitable measure:

As indicated earlier, the setting period  $\beta$  of oscillating heats can be calculated direct from the frequency of the kinetic reaction sound absorption maximum (cf. equation 104e), when, according to figures 1c and 3b, TM 1268, the damping constant  $\gamma l$  referred to the wave length is plotted against the logarithm of the frequency  $f$ . Correctly speaking, only the portion  $\gamma_{Ch}$  of the sound dispersion due to kinetic reaction may really be applied, and not the experimentally defined damping constant  $\gamma$ , which also contains the friction and heat conductivity effects; for according to (148) and (204) the assumption of an additivity for the individual damping effects gives

$$\gamma = \gamma_{Ch} + \frac{(2\pi f)^2}{2a_o^3} \left[ \frac{4v}{3} + (\kappa - 1)\tau \right] + \frac{\sqrt{\pi} [\sqrt{v} + (\kappa - 1)\sqrt{\tau}]}{ra_o} \quad (210)$$

hence

$$\gamma l = \underbrace{\gamma_{Ch} l}_{\substack{\text{curve} \\ \text{with} \\ \text{max-} \\ \text{imum}}} + \underbrace{\frac{2\pi^2 f}{a_o^2} \left[ \frac{4v}{3} + (\kappa - 1)\tau \right]}_{\substack{\text{monotonic rising} \\ \text{curve}}} + \underbrace{\frac{\sqrt{\pi} [\sqrt{v} + (\kappa - 1)\sqrt{\tau}]}{r\sqrt{f}}}_{\substack{\text{monotonic abating} \\ \text{curve}}} \quad (211)$$

and therefore

$$\frac{\partial(\gamma l)}{\partial \ln f} = \frac{\partial(\gamma_{Ch} l)}{\partial \ln f} + \frac{2\pi^2 f}{a_o^2} \left[ \frac{4v}{3} + (\kappa - 1)\tau \right] - \frac{\sqrt{\pi} [\sqrt{v} + (\kappa - 1)\sqrt{\tau}]}{2r\sqrt{f}} \quad (212)$$

The maximum of the experimentally accessible  $\gamma l$  curve is shifted relative to the maximum of the theoretically interesting  $\gamma_{Ch} l$ -curve, that is:

At preponderate R-W longitudinal damping, the  $\gamma l$ -maximum lies at a higher frequency  $f$  than the  $\gamma_{Ch} l$ -maximum.

At preponderate R-W lateral damping, the  $\gamma l$  maximum lies at a lower frequency than the  $\gamma_{Ch} l$ -maximum.

With equations (210) to (212) the location of the theoretically interesting  $\gamma_{Ch}^2$  maximum could be computed from the experimental  $\gamma^2$ -maximum. Admittedly, this correction would not take care of other damping effects, such as those due to roughness or porosity of the wall, since Kirchhoff's calculation was based upon a smooth and tight pipe wall.

## VI. SUPERPOSITION OF INCOMPLETE OSCILLATION EXCITATION AND INCOMPLETE ADJUSTMENT OF THE DISSOCIATION EQUILIBRIUMS IN THE ACOUSTIC FIELD

In this section, two questions are involved:

1. The extent to which the theory should be extended, when not only the dissociation equilibria, but also the heat of oscillation can no longer follow the sound frequency, so that kinetic reaction "dissociation dispersion," as well as "oscillation dispersion," occurs.
2. The eventual disturbances due to oscillation dispersion to be expected in sound measurements in the high-temperature zone.

The first question is answered comparatively quickly. In the original equations [(41)] to [(46)], only [(45)] contains the heat capacity  $C_p$ , or more accurately, the expression  $C_p \frac{dT}{dt}$ . Now, when the inner degrees of freedom of oscillation are able to follow the sound frequency only incompletely, to each one may be coordinated a separate inside temperature  $T_{i\lambda}$ , so that [(45)] becomes

$$\left( C_{pa} \frac{dT}{dt} + \sum_{\lambda} C_{i\lambda} \frac{dT_{i\lambda}}{dt} \right) - v \frac{dp}{dt} - \sum_m w_m \frac{dz_m}{dt} = 0 \quad (213)$$

The inside temperatures  $T_{i\lambda}$  are gradually assimilated to the outer "tangible temperature"  $T$ , and correspond to the equation

$$\left\| \frac{dT_{i\lambda}}{dt} = \frac{T - T_{i\lambda}}{\beta\lambda} \right. \quad (214)$$

where  $\beta_\lambda$  is the average adjusting period<sup>15</sup>. There are as many of these equations as there are different adjusting periods  $\beta_\lambda$ . Fortunately, one single adjusting period has been sufficient up to now, even for molecules with several different normal oscillations, where different  $\beta_\lambda$ -values were suspected. The equations [(47)] hold for  $T_{1\lambda}$  in the periodic field of sound as well as for  $T$ , hence

$$T_{1\lambda} = T_0 + \delta T_{1\lambda}, \text{ with } \delta T_{1\lambda} = \operatorname{Re} \left\{ \underline{T}_{1\lambda} e^{gx+ht} \right\} \quad (215)$$

and therefore by (214)

$$\underline{T}_{1\lambda} = \frac{\underline{T}}{1 + h\beta_\lambda} \quad (216)$$

The elimination of  $T_{1\lambda}$  from (213) and (216) leaves

$$\left( C_{pa} + \sum_{\lambda} \frac{C_{1\lambda}}{1 + h\beta_\lambda} \right) \underline{T} - v_p - \sum_m^m W_m \underline{z}_m = 0 \quad (217)$$

The previous final formulas, especially equation [(70)], remain the same, except for the replacement of  $C_p$  by  $C_{pa} + \sum_{\lambda} \frac{C_{1\lambda}}{1 + h\beta_\lambda}$ . Accordingly the  $\kappa$  introduced by [(19)] is complex, hence

$$(\kappa - 1) \left[ C_{pa} + \sum_{\lambda} \frac{C_{1\lambda}}{1 + h\beta_\lambda} \right] = \kappa \underline{NR}$$

or

$$\left\| \kappa = \frac{C_{pa} + \sum_{\lambda} \frac{C_{1\lambda}}{1 + h\beta_\lambda}}{C_{va} + \sum_{\lambda} \frac{C_{1\lambda}}{1 + h\beta_\lambda}} \right\| \text{ with } h = 2\pi f \cdot i \quad (218)$$

when writing  $\underline{NR} = C_{pa} - C_{va}$ .

<sup>15</sup>Schaefer, Kl., Ztschr. physikal. Chem. B 46, pp. 212 to 228, 1940.

On considering only one adjustment period  $\beta$  and no further dissociation reactions, the expressions [(18)] as well as [(22)] to [(24)] become zero and equation [(70)] becomes

$$\begin{aligned}\frac{p_o}{p_r} &= \kappa = 1 + \frac{NR}{C_{va} + \frac{C_1}{1 + h\beta}} \\ &= 1 + \frac{R(1 + i \cdot 2\pi f\beta)}{C_a(1 + i \cdot 2\pi f\beta) + C_1}\end{aligned}\quad (219)$$

hence, exactly the same equation (104a) again, as, of course, expected.

The second question, whether perceptible disturbances due to "oscillation dispersion" are to be expected, could be answered exactly if the temperature relationship of the characteristic adjustment periods  $\beta_\lambda$  up to the corresponding temperatures were known. But, unfortunately, this is known only to about 673° K. Interpolation up to 2600° K is, naturally, questionable. Nevertheless, it is attempted even at the risk of it not being permissible.

The number of collisions which must be exerted on a molecule to transfer its oscillation quantum to translation energy ranges between  $z^* = 10^2$  and  $10^7$ . If the molecule collides  $10^{10}$  times per second (NPT conditions) the adjustment period amounts to  $\beta \approx 10^{-8}$  to  $10^{-3}$  seconds. The characteristic frequency for the maximum of the oscillation absorption would thus be about  $f_m \approx \frac{1}{2\pi\beta} \approx 10^7$  to  $10^2$  cps according to equation (104e). The first value applies approximately to CO<sub>2</sub>, in which the conversion of translation to oscillation energy was facilitated by added H<sub>2</sub>O, the last value holds, in order of magnitude, for purest, dry O<sub>2</sub>.

The temperature relationship of the number of collisions  $z^*$  required for abating the oscillation was studied very exhaustively by Eucken and associates. They found<sup>16</sup>:

1. In those cases, where  $z^*$  is a small number, hence where the abatement of the oscillations is already very easy, the temperature relationship of  $z^*$  is rather small and particularly not in any definite direction.

<sup>16</sup>Eucken, A. and K  chler, L., Ztschr. techn. Physik 19, 1938, pp. 517 to 521: Summarizing Lecture at the Physicists' Conference in Baden-Baden, 1938.

2. In those cases where  $z^*$  is large, hence where the abatement is difficult,  $z^*$  decreases monotonically with rising temperature.

At this point the first case is less interesting, since according to the foregoing the dissociation dispersion measurements will be made at lower frequencies than the earlier oscillation dispersion measurements. The second case of great number of collisions ( $z^* \approx 10^4$  to  $10^7$ ) occurs chiefly on pure gases. Examples are presented in figure 5, where  $z^*$  is plotted against  $\frac{10^3}{T}$ . Allowing for the scattering of the test points, especially on comparison of the various authors, the test series can still be approximated by straight lines. From their slope, the effective heats of activation  $g$  can be computed (expressed in wave numbers (dimension =  $\text{cm}^{-1}$ ) at the curves). Strange to say, the  $g$  values coincide fairly closely with the lowest normal oscillations of the respective molecule, as is evident from Table 9.

This could be interpreted with the assumption that a molecule excited in its normal oscillation can, at collision with another molecule, lose its oscillation quantum only when the two colliding molecules together have an additional minimum energy of the magnitude of an oscillation quantum. Such an interpretation immediately raises, of course, the question whether this additional energy necessary as heat of activation is to be regarded as relative energy of the two colliding molecules, or whether the second colliding molecule, which forces the first colliding molecule to yield its oscillation energy as translation energy, might not itself possess an identically large oscillation quantum. For the present, further speculations are useless, so long as no additional experimental data are available. But it will be shown in what ratio the  $z^*$  required for oscillation abatement would be reduced for pure  $\text{O}_2$ , if such an agreement between oscillation quantum and effective heat of activation existed for it, too, and if interpolation to  $2600^\circ \text{K}$  were permissible. The normal oscillation quantum of  $1580 \text{ cm}^{-1} = 4500 \text{ cal/mol}$  would give

$$\frac{z^*_{2600^\circ \text{K}}}{z^*_{293^\circ \text{K}}} = 10^{-\frac{4500 \times 2307}{4.573 \times 293 \times 2600}} = 10^{-2.98} \quad (220)$$

Thus the number of collisions required for abating the oscillation would drop by 0.3 percent, the characteristic frequency of the oscillation dispersion zone increase by 0.3 percent, or from  $10^2$  to  $10^5$  cps. But with it even the most difficult excitable and abatable  $\text{O}_2$  would

interfere rather little in high-temperature acoustic measurements. (First reason.) Naturally, this extrapolation is no longer uncertain.

But there is also a second reason that speaks against excessive disturbances by incomplete oscillation adjustment of  $O_2$  in the high-temperature zone. Eucken and his associates observed again and again that the adjustment of the oscillation heat of a molecule is very much facilitated even when the gas contains the least traces of foreign molecules capable of forming quasi-chemical combination complexes with the basic gas. But such additional substances in the high-temperature zone are the atoms, so that the appearance of the following collision complexes can well be reckoned with;



$O_2 \cdot O$  would be a quasi-ozone molecule.<sup>17</sup>

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<sup>17</sup>The amount of  $O_3$  present in the thermodynamic equilibrium can be estimated by the equation

$$\lg \frac{p_{O_3}}{(p_{O_2})^{3/2}} = \frac{-7.44 \times 10^3}{T} - 3.60 \quad \text{with} \quad [p_{O_2}] = [p_{O_3}] = \text{Atm.} \quad (222)$$

which was obtained by using the values  $\Delta C_{298} = 38.9$  and  $\Delta H_{298} = 34.0$  kcal for the reaction  $\frac{3}{2}O_2 \rightarrow O_3$  (Chem. Manual 1939, III, 238). For  $2600^\circ K$  and 1 atm. total pressure with  $p_{O_2} = 0.078$ , it would give  $\frac{p_{O_3}}{p_{O_2}} = 1.03 \times 10^{-7}$ , compared to  $\frac{p_O}{p_{O_2}} = 0.087$  in Table 4.

In actual measurements it would, of course, have to be always ascertained that the dissociation dispersion to be studied was not accompanied by any oscillation dispersion. This is most easily done by numerically comparing the experimental sound data with the values computed by [(70)] and [(78)] or [(79)], after correction for the R-W damping and eventual departures from the ideal gas law.<sup>18</sup>

The lowest sound velocity is obtained when the dissociation, as well as the adjustment of the oscillation heat, is able to follow the sound frequency completely. If one of the two processes ceases to follow, the sonic velocity must be higher. Then it will be checked whether the value of the complete oscillation adjustment but of the incomplete dissociation equilibrium adjustment is reached anywhere, or vice versa, or finally whether in a single, no longer dissolvable, sound-dispersion stage both kinetic processes lose their adjusting capacity on the impressed oscillation period simultaneously. The last case would naturally be least desired. Unfortunately, it occurs in the  $N_2O_4$  dissociation, which was investigated several times at room temperature, without definite result.<sup>19</sup> But in this instance, a third reason can be given which likewise militates against abnormal disturbances by oscillation dispersion in the high-temperature zone, namely, the ratio of dissociation energy to oscillation quantum in the  $N_2O_4$  tests at room temperature was about  $14:2 = 7$ , while in the dissociation reactions of interest in the high-temperature zone the ratios are most likely to range at  $100:2 = 50$ . The transfer of such a many times greater dissociation energy to a molecule is, however, considerably harder; at least, it will take more stages than that of the relatively low oscillation quantum; hence the first process is in all probability slower also. Thus, however, the zone of the oscillation dispersion would lie at higher sound frequencies than that of the dissociation dispersion.

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<sup>18</sup>Eucken and Becker (Ztschr. physikal. chem. B27, 1934, pp. 219-234) have given a correction for the departure from the ideal gas law for oscillation dispersion measurements. But whether this correction holds for dissociation dispersion measurements as well remains an open question. The departures from the ideal gas law effect: (1) an extension of the equation of state by the second Virial coefficient and (2) an extension of the equation of energy (9) by the term  $\left(\frac{\partial H}{\partial p}\right)_{TN_j} \cdot \delta p$  and (3) the introduction of activation coefficients in the law of mass effect [(10)] and equation [(62)]. Point 3 was not taken into consideration in Eucken's correction, though it should be unimportant even in oscillation dispersion measurements, since the activation coefficients of an oscillating and a nonoscillating molecule are the same. But it is different for the excitation of an electron term, since such a molecule exerts, for example, other force effects outward, by reason of increased polarizability.

<sup>19</sup>Kneser, H. O., and Gauler, O., Physikal. Ztschr. 37, 1936, pp. 677 to 684.



## VII. SIGNIFICANCE OF THE HELMHOLTZ RESONATOR IN SOUND-DISPERSION MEASUREMENTS

The remaining question concerns the method of making such sound measurements, especially in the audible frequency range and at high temperatures. By the usual method of standing waves in the pipe (acoustic interferometer) generally applied to ultrasonic measurements up to now only  $10^4$  to  $10^5$  cps are involved. At  $f = 10^3$  cps the wave length  $\lambda$  is already 77 cm according to Table 6, (TM 1268) so that the test chamber to be uniformly tempered would have to be 50 cm long at least for a single half wave. And even if this were possible, it would render a frequency range of no more than two powers of ten, that is, from  $10^3$  to  $10^5$  cps. That is not very much considering the dissociation dispersion curves reproduced in figures 1 and 3, TM 1268. But the absolute uniform tempering of a space 50 cm in length to  $\frac{\delta T}{T} < 10^{-3}$  is hardly possible without greater outlay, since blocks of copper or aluminum are, naturally, unsuitable at those high temperatures. It calls for ceramic materials with low thermal conductivity. Whether the heat exchange by mediation can balance this defect remains to be seen.

To sum up, it calls for a method of finding the sonic velocity where the actual test space is smaller by an order of magnitude than the wave length. This requirement is met by the Helmholtz resonator, which, strange to say, has never been used for sound-dispersion measurements in the audible range.

The Helmholtz resonator consists of a hollow ball with a cylindrical open neck. The natural frequency  $f_0$  follows the equation

$$f_0 = \frac{a}{2\pi} \sqrt{\frac{C}{S}} \quad (223)$$

where  $a$  is the velocity of sound,  $S$  the volume of the resonator, and  $C$  the so-called acoustic conductivity of the resonator throat.

Lord Rayleigh's representation (footnote 11, p. 170 ff.) is particularly interesting. If  $S$  is a sphere of  $2R$  diameter, and the neck is a circular cylinder of  $2r$  inside diameter and of length  $L$

$$S = \frac{4\pi}{3} R^3 \quad \text{and} \quad C = \frac{\pi r^2}{L + \frac{\pi r}{2}} \quad (224)$$

Expressing the width and length of the neck nondimensionally by the diameter of the resonator ball, that is, putting

$$\frac{2r}{2R} = \rho \quad \text{and} \quad \frac{L}{2R} = \sigma \quad (225)$$

gives

$$f_0 = \frac{a\rho}{4\pi R} \sqrt{\frac{3}{2\sigma + \frac{\pi\rho}{2}}} \quad (226)$$

Of chief interest is the ratio of resonator ball diameter to resonance wave length:

$$\left\| \frac{2R}{l_0} = \frac{2Rf_0}{a} = \frac{\rho}{2\pi} \sqrt{\frac{3}{2\sigma + \frac{\pi\rho}{2}}} \right. \quad (227)$$

For the plausible numerical values  $\rho = 0.2$  and  $\sigma = 0.5$ , it results in

$$\frac{2R}{l_0} = \frac{0.2}{2\pi} \sqrt{\frac{3}{1.314}} = 0.048 \quad (228)$$

The ball diameter of Helmholtz's resonator would thus be only about 5 percent of the wave length, while for a standing wave in a pipe closed at both ends this must be at least a half wave length long. Helmholtz's resonator would therefore be of ten times smaller dimensions than required by the method of standing wave in a pipe (acoustic interferometer).

Owing to the radiation damping, the resonance curve of the Helmholtz resonator has a finite half-width value  $2\delta$ . It can be made nondimensional with the natural frequency  $f_0$ :

$$\left\| \frac{2\delta}{f_0} = \frac{1}{2\pi} \sqrt{\frac{c^3}{8}} = \frac{\rho^3}{4} \sqrt{\frac{3}{\left(2\sigma + \frac{\pi\rho}{2}\right)^3}} \right. \quad (229)$$

with the previous values  $\rho = 0.2$  and  $\sigma = 0.5$  it gives

$$\frac{2\delta}{f_0} = \frac{8 \times 10^{-3}}{4} \sqrt{\frac{3}{1.3143}} = 2.3 \times 10^{-3} \quad (230)$$

The resonance acuity is not bad. It is likely to be reduced by the additional damping effects of friction and heat conductivity.

This disturbance cannot be expressed numerically. But if it should be small only, a reduction of the relative throat width, that is, a reduction of  $\frac{2R}{l_0}$  and  $\frac{2\delta}{f_0}$  still further by transition to still smaller  $\rho$  values at constant  $\sigma$ , might be recommended because  $\rho$  affects the expressions (227) and (229) in the same sense.

Obviously, a number of problems must be solved experimentally and theoretically before sound-dispersion measurements in the high-temperature zone can be satisfactorily carried out and interpreted. But the kinetic explanation of the dissociation reactions under extreme temperature conditions is not to be evaded, if one day it is desirable to understand the chemical processes involved in flames or detonating waves.

#### SUMMARY

1. A generally applicable formula [(equation 29)] is derived for the differential isentropic exponent  $m$  in dissociating gases:

$$m = \frac{-V}{p} \left( \frac{\partial p}{\partial V} \right)_s \quad \text{in the isentropic } pV^m = \text{const.}, \text{ complete equilibrium at}$$

every instant of the phase change being postulated. The number and kind of dissociation equilibriums are arbitrary.

2. The kinetically delayed balance of chemical gas equilibrium (reactions dissociation and recombination) in the field of sound is dealt with. A generally applicable interpretation formula for sound-dispersion tests is obtained: equation [(70)], together with equations [(78)] and [(79)]. In contrast to the premises of Einstein and Kneser, the formula was derived without special assumptions regarding the usually still unknown kinetics of the adjustment processes. In the new formula, any desired amount of reaction possibilities can be taken into consideration.

3. The sound-dispersion measurements primarily afford the speeds of the thermodynamically unrelated over-all reactions. The elementary

reactions defining them follow secondarily by additional assumptions, as by the principle of microscopic reversibility, for instance. The concept of "step-wise retardation" (retardation by up-position lock) at which the thermodynamic equilibrium is maintained by reaction cycles (one path track) is ruled out.

4. The theoretical cases of sound dispersion already treated by other authors such as the incomplete equilibrium adjustment of a monomolecular dissociating and bimolecular recombining substance (Einstein), or the incomplete adjustment of a single degree of freedom of oscillation (Kneser), for instance, appear as special cases in the final formula [(70)] of the present report.

5. The differential isentropic exponents  $m$  for two high-temperature systems, namely, the  $O_2$  and  $CO_2$  dissociation, are computed and the presumable sound-dispersion zone for  $2600^\circ K$  and 1 atm. total pressure estimated. The general character of sound dispersion caused by kinetic reaction, that is, the frequency relationship of the sonic velocity  $a$ , of the damping constant  $\gamma$  referred to unit length (cm) for the sound amplitude and of the damping constant  $\gamma l$  referred to the wave length  $l$  are discussed on the basis of the obtained curves.

6. At  $2600^\circ$  absolute and 1 atm. total pressure,  $CO + O + M \rightarrow CO_2 + M$  as well as  $CO + O_2 \rightarrow CO_2 + O$  should proceed as elementary reaction; the second reaction could even be decisive.

7. The sound dispersion due to friction and heat conductivity (R-W damping), originally developed by Kirchhoff, is discussed and contrasted with the dispersion due to kinetic reaction. An irreversible exchange of momentum, energy and even particle types, corresponding to the friction, heat conductivity, and diffusion, can take place along the direction of propagation of sound, as well as crosswise to it. The latter occurs in the pipe of finite inside width.

Treated separately in the plane laterally unlimited sound wave are:

- (a) The R-W longitudinal damping
- (b) The coupling of kinetic-reaction damping and R-W longitudinal damping
- (c) The coupling of kinetic-reaction damping, R-W longitudinal damping, and diffusion effect

For the cylindrical pipe the study included

- (a) The R-W lateral damping
- (b) Comparison of the  $\gamma$  values of pure kinetic-reaction damping, of pure R-W longitudinal damping, and pure R-W lateral damping

8. From the numerical values of the sound absorption, it is estimated that sound-dispersion measurements above  $10^5$  cps in the high-temperature zone will not be possible until sound of specified frequencies can be produced in the hot test chamber itself.

9. The total damping constant  $\gamma_l$  referred to wave length  $l$  has a maximum only in kinetic-reaction dispersion, and that only at a certain frequency. It is largely defined by the adjusting period of the chemical equilibriums but it can also be shifted by the R-W damping. Preponderant R-W longitudinal damping shifts toward higher, preponderant R-W lateral damping toward lower frequencies.

10. The new formula for the dissociation dispersion equation [(70)] is extended to include the case where the internal degrees of freedom of oscillation of the molecules can no longer follow the sound frequencies (oscillation dispersion): equation [(128)]. Three unrelated arguments make the appearance of disturbances due to oscillation dispersion in the high-temperature zone rather doubtful in an investigation of dissociation reactions.

11. The continuously increasing wave length imposes a limit toward low frequencies on the sound-dispersion zone accessible to experimental measurement. With the Helmholtz resonator, it probably will be possible to make sound-dispersion measurements even below  $10^3$  cps, because the dimensions of the test chamber to be tempered uniformly (up to about 1 percent exact) need to be only  $1/10$  to  $1/20$  of the wave length.

Translated by J. Vanier  
National Advisory Committee  
for Aeronautics.

TABLE 7

ESTIMATED SOUND DISPERSION IN PURE CO<sub>2</sub> AT 2600° K AND 1 ATMOSPHERE (CASE II)

Ch = effect of incomplete chemical equilibrium (R = friction effect)

W = heat-conductivity effect

(D = diffusion effect)

No.	Calculation process	$\tau$ (s <sup>-1</sup> )	$a \times 10^{-4}$ (cm s <sup>-1</sup> )	$\gamma$ (cm <sup>-1</sup> )	$\gamma^2$	$e^{-10\gamma}$	$e^{-20\gamma}$
1	Ch by equation [(70)], [(78)], [(79)]	$1 \times 10^5$	7.770	$1.218 \times 10^{-1}$	$9.46 \times 10^{-2}$	0.2958	0.0875
		$1 \times 10^6$	7.932	$3.539 \times 10^{-1}$	$2.808 \times 10^{-2}$	0.02904	$8.433 \times 10^{-4}$
		$1 \times 10^7$	7.938	$3.605 \times 10^{-1}$	$2.861 \times 10^{-3}$	0.02719	$7.393 \times 10^{-4}$
2	R + W by Kirchhoff [(146)]	$1 \times 10^5$	7.941	$2.365 \times 10^{-3}$	$1.878 \times 10^{-3}$	0.9766	0.9537
		$1 \times 10^6$	7.941	$2.365 \times 10^{-1}$	$1.878 \times 10^{-2}$	0.09395	$8.827 \times 10^{-3}$
		$1 \times 10^7$	7.939	23.69	$1.880 \times 10^{-1}$	$1.305 \times 10^{-103}$	$1.703 \times 10^{-206}$
3	Ch + R + W from No. 1 and No. 2 $\gamma$ -values added	$1 \times 10^5$		$1.2416 \times 10^{-1}$			
		$1 \times 10^6$		$5.904 \times 10^{-1}$			
		$1 \times 10^7$		24.050			
4	Ch + R + W by [(183)]	$1 \times 10^5$	7.772	$1.241 \times 10^{-1}$	$9.647 \times 10^{-2}$	0.2891	$8.358 \times 10^{-2}$
		$1 \times 10^6$	7.933	$5.900 \times 10^{-1}$	$4.680 \times 10^{-2}$	$2.739 \times 10^{-3}$	$7.502 \times 10^{-6}$
		$1 \times 10^7$	7.939	24.00	$1.905 \times 10^{-1}$	$5.877 \times 10^{-105}$	$3.454 \times 10^{-209}$
5	Ch + R + W + D by eq. [(200)]	$1 \times 10^5$	7.772	$1.241 \times 10^{-1}$	$9.647 \times 10^{-2}$	0.2891	$8.358 \times 10^{-2}$
		$1 \times 10^6$	7.933	$5.900 \times 10^{-1}$	$4.680 \times 10^{-2}$	$2.739 \times 10^{-3}$	$7.502 \times 10^{-6}$
		$1 \times 10^7$	7.939	24.00	$1.905 \times 10^{-1}$	$5.877 \times 10^{-105}$	$3.454 \times 10^{-209}$

$$\tau = 1 \times 10^5 \quad \frac{t_p}{t_g} = \frac{a^2}{4D\tau} = 2.25 \times 10^3$$

$$\begin{array}{cc} 1 \times 10^6 & 2.25 \times 10^2 \\ 1 \times 10^7 & 2.25 \times 10^1 \end{array}$$

TABLE 8

THE KIRCHHOFF-HELMHOLTZ SOUND DISPERSION CAUSED SOLELY BY THE FINITE PIPE WIDTH (SMOOTH AND NONPOROUS WALL)

IN PURE CO<sub>2</sub> AT 2600° K AND 1 ATMOSPHERE TOTAL PRESSURE

R-W Internal Damping Allowed for, Sound Dispersion Due to Kinetic Reaction and  
to R-W Longitudinal Damping Disregarded.

$$\nu = 3.9 \text{ cm}^2/\text{sec}; \tau = 4.6 \text{ cm}^2/\text{sec}; \kappa = 1.175; \sqrt{\nu + (\kappa - 1)/\tau} = 2.35; a_0 = 7.941 \times 10^4 \text{ cm/sec}$$

2r (cm)	f = 1 × 10 <sup>3</sup> cps				f = 1 × 10 <sup>5</sup> cps				f = 1 × 10 <sup>7</sup> cps			
	$\frac{a_0 - a}{a_0}$	$\gamma$ (cm <sup>-1</sup> )	e <sup>-10γ</sup>	e <sup>-20γ</sup>	$\frac{a_0 - a}{a_0}$	$\gamma$ (cm <sup>-1</sup> )	e <sup>-10γ</sup>	e <sup>-20γ</sup>	$\frac{a_0 - a}{a_0}$	$\gamma$ (cm <sup>-1</sup> )	e <sup>-10γ</sup>	e <sup>-20γ</sup>
6	6.99 × 10 <sup>-3</sup>	5.53 × 10 <sup>-4</sup>	0.9945	0.9890	6.99 × 10 <sup>-4</sup>	5.53 × 10 <sup>-3</sup>	0.9462	0.8953	6.99 × 10 <sup>-5</sup>	5.53 × 10 <sup>-2</sup>	0.5752	0.3309
2	2.096 × 10 <sup>-2</sup>	1.659 × 10 <sup>-3</sup>	.9835	.9673	2.096 × 10 <sup>-3</sup>	1.659 × 10 <sup>-2</sup>	.8471	.7176	2.096 × 10 <sup>-4</sup>	1.659 × 10 <sup>-1</sup>	.1903	3.621 × 10 <sup>-2</sup>
0.6	6.99 × 10 <sup>-2</sup>	5.53 × 10 <sup>-3</sup>	.9462	.8953	6.99 × 10 <sup>-3</sup>	5.53 × 10 <sup>-2</sup>	.3752	.3309	6.99 × 10 <sup>-4</sup>	5.53 × 10 <sup>-1</sup>	3.966 × 10 <sup>-3</sup>	1.573 × 10 <sup>-5</sup>
.2	2.096 × 10 <sup>-1</sup>	1.659 × 10 <sup>-2</sup>	.8471	.7176	2.096 × 10 <sup>-2</sup>	1.659 × 10 <sup>-1</sup>	.1903	3.621 × 10 <sup>-2</sup>	2.096 × 10 <sup>-3</sup>	1.659	6.24 × 10 <sup>-8</sup>	3.894 × 10 <sup>-15</sup>

TABLE 9  
NORMAL OSCILLATIONS AND EFFECTIVE HEAT OF ACTIVATION  $q$  FOR ABATEMENT  
OF THE OSCILLATION IN PURE GASES

Gas	Normal oscillations according to Sponer (molecule spectra 1935) in $\text{cm}^{-1}$	Heat of activation $q$		Acoustic measurement by
		$\text{cm}^{-1}$	cal/mol	
$\text{Cl}_2$	$\omega_e = 564.9$	1024 555	2911 1578	A. Eucken and R. Becker <sup>1</sup>
$\text{CO}_2$	$\left. \begin{array}{l} v_u = 2350.1 \\ v_t \\ 2^2\omega_u \end{array} \right\} = \left\{ \begin{array}{l} 1285.8 \\ 1388.4 \end{array} \right.$ undisturbed level $b_1$ 1336 $2\omega_u = 667.5$	588 836	1674 2379	A. Eucken and R. Becker <sup>1</sup> A. Eucken and E. Nümann <sup>2</sup> L. Küchler <sup>3</sup>
$\text{N}_2\text{O}$	$\left. \begin{array}{l} v_t(1) = 2224.1 \\ v_t(2) = 1285.4 \end{array} \right\}$ $2\omega = 589.0$	676 447	1921 1271	A. Eucken and H. Jaacks <sup>4</sup> A. Eucken and E. Nümann <sup>2</sup>
$\text{CO}$	$\left. \begin{array}{l} v_t(1) = 2079 \\ v_t(2) \\ 2^2\omega \end{array} \right\} = \left\{ \begin{array}{l} 859 \\ 1051 \end{array} \right.$ $2\omega = 527$	521	1481	A. Eucken and S. Aybar <sup>5</sup>
$\text{CH}_4$	$\left. \begin{array}{l} v_t \\ 2^2\omega \end{array} \right\} = \left\{ \begin{array}{l} 2915 \\ 3071 \end{array} \right.$ $3\omega = 1304$ $2\omega = 1520$ $3v = 3022$	635	1806	A. Eucken and S. Aybar <sup>5</sup>

<sup>1</sup>A. Eucken and R. Becker, Ztschr. physikal. Chem. B 27, pp. 235-262 (1934).

<sup>2</sup>A. Eucken and E. Nümann, Ztschr. physikal. Chem. B 36, pp. 163-183 (1937).

<sup>3</sup>L. Küchler, Ztschr. physikal. Chem. B 41, pp. 199-214 (1938).

<sup>4</sup>A. Eucken and H. Jaacks, Ztschr. physikal. Chem. B 30, pp. 85-112, (1935).

<sup>5</sup>A. Eucken and S. Aybar, Ztschr. physikal. Chem. B 46, pp. 195-211 (1940).



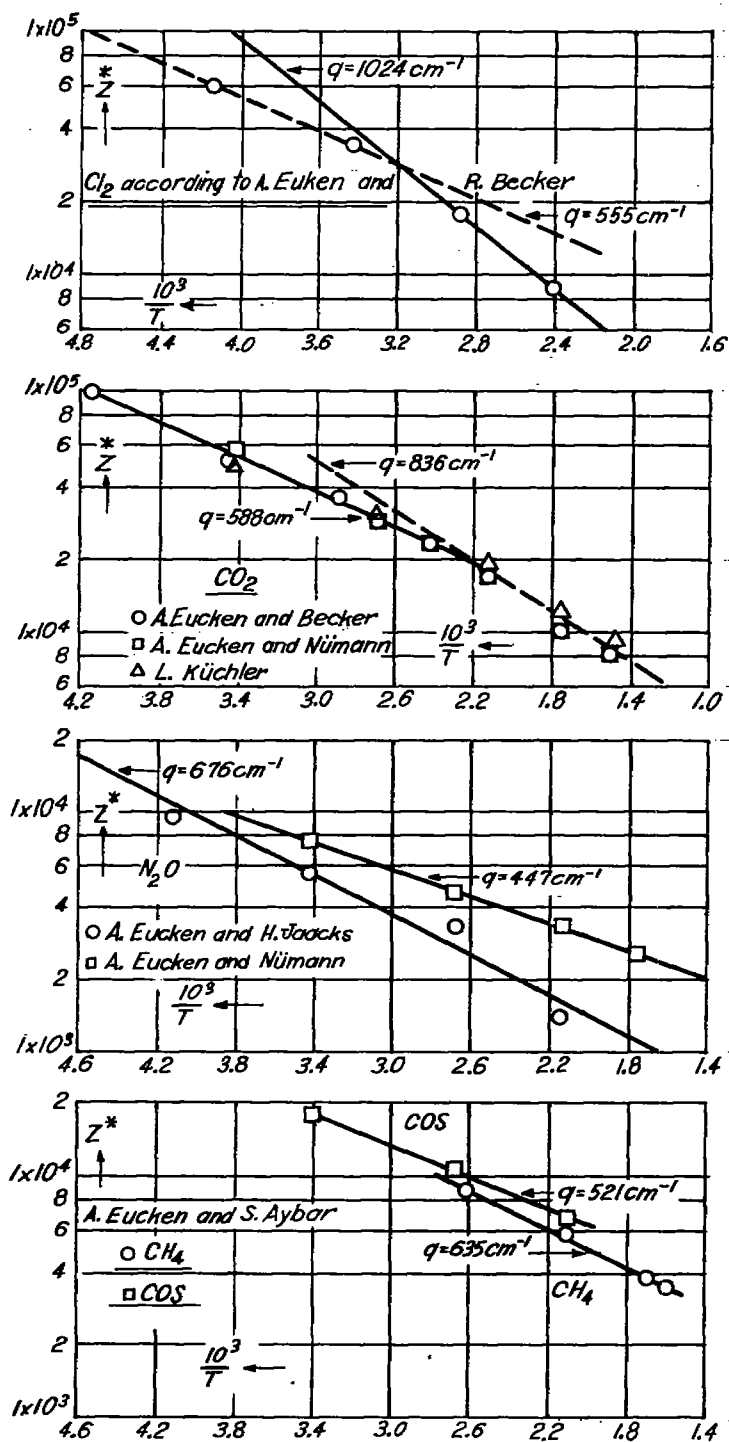


Figure 5.- The number of collisions  $z^*$  which a molecule sustains before yielding its oscillation quantum plotted against the reciprocal temperature (measurements by Eucken and associates).

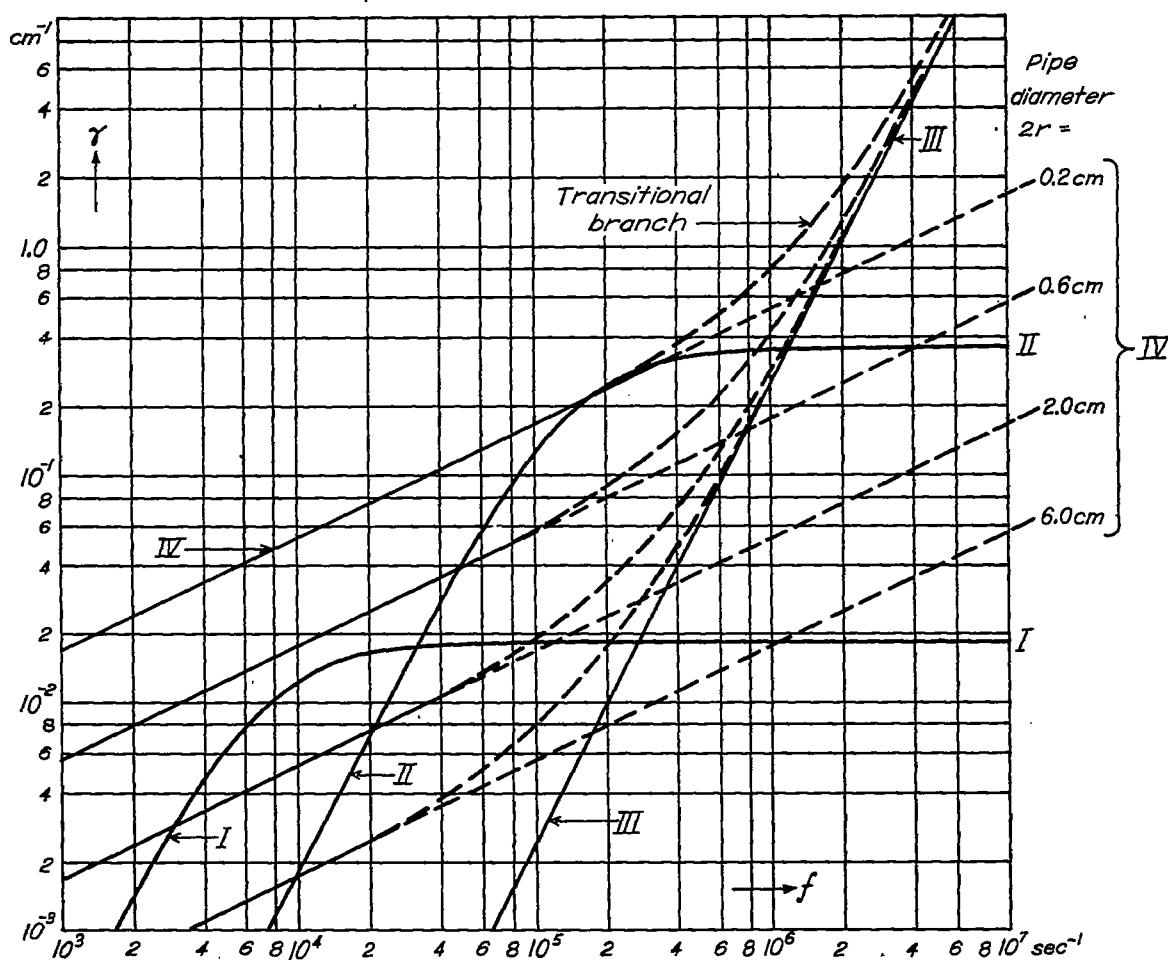


Figure 4.- Damping coefficient  $\gamma$  for the sound amplitude: I and II = cases of pure kinetic reaction sound dispersion for the  $\text{CO}_2$  dissociation (p. 43, TM 1268), III = pure R-W longitudinal damping, IV = pure R-W lateral damping in the smooth pipe.